PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C10G 45/64 A1

(11) International Publication Number: WO 90/11338

(43) International Publication Date: 4 October 1990 (04.10.90)

(21) International Application Number: PCT/US90/00933

(22) International Filing Date: 16 February 1990 (16.02.90)

(30) Priority data:
325,735 20 March 1989 (20.03.89) US

(71) Applicant: MOBIL OIL CORPORATION [US/US]; 150 East 42nd Street, New York, NY 10017 (US).

(72) Inventors: NEMET-MAVRODIN, Margaret ; 503 Garwood Drive, Cherry Hill, NJ 08003 (US). SOTO, Jorge, Luis ; 7 Charleston Court, Sewell, NJ 08080 (US).

(74) Agents: HOBBES, Laurence, P. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037 (US).

(81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), NO, SE (European patent).

Published
With international search report.

(54) Title: PROCESS FOR THE CONVERSION OF C_2-C_{12} PARAFFINIC HYDROCARBONS TO PETROCHEMICAL FEEDSTOCKS

(57) Abstract

A process is disclosed for the conversion of C_2-C_{12} paraffinic hydrocarbons to more valuable petrochemical feedstocks including C_2-C_4 olefins and C_6-C_8 aromatics in the presence of a composite catalyst comprising a binder and at least one zeolite having a Constraint Index of between 1 and 12, the composite catalyst having an alpha value of greater than 5 and less than 33. It has been found that yields of valuable C_2-C_4 olefins and C_6-C_8 aromatics are increased by maintaining the composite catalyst alpha value within the claimed range.

+ See back of page

DESIGNATIONS OF "DE"

Until further notice, any designation of "DE" in any international application whose international filing date is prior to October 3, 1990, shall have effect in the territory of the Federal Republic of Germany with the exception of the territory of the former German Democratic Republic.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria
AU	Australia
BB	Barbados
BE	Belgium
BF	Burkina Fasso
BG	Bulgaria
BJ	Benin
BR	Brazil
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CM	Cameroon
DE	Germany, Federal Republic of
DK	Denmark
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
HU	Hungary
IT	Italy
JP	Japan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
LI	Liechtenstein
LK	Sri Lanka
LU	Luxembourg
MC	Monaco
MG	Madagascar
ML	Mali
MR	Mauritania
MW	Malawi
NL	Netherlands
NO	Norway
RO	Romania
SD	Sudan
SE	Sweden
SN	Senegal
SU	Soviet Union
TD	Chad
TG	Togo
US	United States of America

PROCESS FOR THE CONVERSION OF C_2-C_{12} PARAFFINIC HYDROCARBONS TO PETROCHEMICAL FEEDSTOCKS

This invention relates to the co-production of aromatics, especially C_6-C_8 aromatics, and olefins, especially C_2-C_4 olefins, from paraffinic feedstocks (e.g. Udex raffinate) by converting these feedstocks in the presence of a medium-pore zeolite catalyst having closely controlled acid activity.

U.S. Patent 3,756,942 to Cattanach discloses a process for converting paraffinic feedstocks over medium-pore zeolites to produce a variety of upgraded hydrocarbon products. The underlying chemistry involved in this conversion is extremely complex, including cracking of paraffins, aromatization of olefins, and alkylation and dealkylation of aromatics. The article "M2 Forming A Process for Aromatization of Light Hydrocarbons", by N. Y. Chen and T. Y. Yan, 25 Ind. Eng. Chem. Process Des. Dev. 151, 1986 provides a general overview of the reactions and mechanisms believed to be involved in such aromatization reactions. Products from the conversion of C_5+ paraffinic feedstocks over medium-pore zeolites such as ZSM-5 include C_6-C_8 aromatics, C_2-C_4 olefins, C_9+ aromatics and C_1-C_3 paraffins. Of these products the C_6-C_8 aromatics and C_2-C_4 olefins are most desired.

C_6-C_8 aromatics, e.g. benzene, toluene, xylene and ethylbenzene, also known collectively as BTX, are valuable organic chemicals, useful both as intermediate feedstocks as well as saleable end products. Since BTX has a high octane value it can be used as a blending stock for making high octane gasoline. In contrast, C_9+ aromatics (i.e. aromatic compounds having at least 9 carbon atoms) tend to have a relatively low octane value.

C_2-C_4 olefins, e.g. ethylene, propylene and butene, are also valuable organic chemicals which can be used to form polymers.

By way of contrast, C_1-C_3 paraffins (i.e. methane, ethane and propane), particularly in admixture, are less valuable chemicals which are generally used for fuel.

From the foregoing, it can therefore well be seen that it would be highly desirable to shift selectivity in a process for upgrading paraffinic feedstreams toward more valuable products including C_6-C_8 aromatics and C_2-C_4 olefins.

The acid catalytic activity of zeolite catalysts, for example, aluminosilicate ZSM-5, is proportional to aluminum content in the framework of the zeolite. The more aluminum in the zeolite framework, the greater the acid catalytic activity of the zeolite, particularly as measured by alpha value. Note the article by Haag et al., "The Active Site of Acidic Aluminosilicate Catalysts," 309 Nature, 589-591 (1985), especially Figure 2 on page 590 thereof. Medium-pore zeolites with very little framework aluminum and correspondingly low acid catalytic activity can be prepared from reaction mixtures containing sources of silica and alumina, as well as various organic directing agents. For example, the Dwyer et al. U.S. Patent 3,941,871 describes the preparation of ZSM-5 from a reaction mixture comprising silica, tetrapropylammonium ions and no intentionally added alumina. The alumina to silica molar ratio of the ZSM-5 produced by this method may be less than 0.005.

U.S. Patent 4,341,748 describes the preparation of ZSM-5 from reaction mixtures which are free of organic directing agents. However, the reaction mixture for making this organic-free form of ZSM-5 is restricted to silica to alumina molar ratios of 100 or less. Consequently, this organic-free synthesis tends to produce ZSM-5 having a relatively high acid catalytic activity (e.g. alpha value) in comparison with zeolites prepared by the method of the Dwyer et al U.S. Patent 3,941,871.

Co-pending U.S. Application 140,360, filed January 4, 1988, cited above and incorporated by reference as if set forth at length herein, disclosed improvement in selectivity toward valuable

C_2-C_4 olefins and C_6-C_8 aromatics by reducing the alpha value of the composite zeolite catalyst. However, until the advent of the present invention, the criticality of maintaining the composite catalyst alpha value within a narrow range has not been appreciated.

It has now been found in accordance with one aspect of the present invention that the selectivity of paraffinic feedstock conversion to C_6-C_8 aromatics and C_2-C_4 olefins in the presence of a medium-pore zeolite catalyst having a Constraint Index of between 1 and 12 is increased by controlling the acid activity of the zeolite within a narrow range of relatively low values.

According to one aspect of this invention there is provided a process for converting a hydrocarbon feedstock comprising at least 75 percent by weight of a mixture of at least two paraffins having from 5 to 10 carbon atoms, the process comprising contacting the hydrocarbon feedstock under sufficient conditions with a catalyst comprising (1) a binder and (2) a zeolite having a Constraint Index of between 1 and 12, the zeolite being in particular an aluminosilicate zeolite, the composite catalyst having an alpha value of greater than 5 and less than 33, preferably 10 to 20, whereby at least 90 percent by weight of the paraffins are converted to a product mixture.

The members of the class of zeolites useful in the process of the present invention have an effective pore size of generally from 5×10^{-7}mm to 8×10^{-7}mm, such as to freely sorb normal hexane. In addition, the structure must provide constrained access to larger molecules. It is sometimes possible to judge from a known crystal structure whether such constrained access exists. For example, if the only pore windows in a crystal are formed by 8-membered rings of silicon and aluminum atoms, then access by molecules of larger cross section than normal hexane is excluded and the zeolite is not of the desired type. Windows of

10-membered rings are preferred, although, in some instances, excessive puckering of the rings or pore blockage may render these zeolites ineffective.

Although 12-membered rings in theory would not offer sufficient constraint to produce advantageous conversions, it is noted that the puckered 12-ring structure of TMA offretite does show some constrained access. Other 12-ring structures may exist which may be operative for other reasons, and therefore, it is not the present intention to entirely judge the usefulness of the particular zeolite solely from theoretical structural considerations.

A convenient measure of the extent to which a zeolite provides control to molecules of varying sizes to its internal structure is the Constraint Index of the zeolite. The method by which the Constraint Index is determined is described in U.S. Patent 4,016,218. U.S. Patent 4,696,732 discloses Constraint Index values for typical zeolite materials.

In a preferred embodiment, the catalyst is a zeolite having a Constraint Index of between 1 and 12. Examples of such zeolite catalysts include ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35 and ZSM-48.

Zeolite ZSM-5 and the conventional preparation thereof are described in U.S. Patent 3,702,886. Other preparations for ZSM-5 are described in U.S. Patents Re. 29,948 (highly siliceous ZSM-5); 4,100,262 and 4,139,600. Zeolite ZSM-11 and the conventional preparation thereof are described in U.S. Patent 3,709,979. Zeolite ZSM-12 and the conventional preparation thereof are described in U.S. Patent 3,832,449. Zeolite ZSM-23 and the conventional preparation thereof are described in U.S. Patent 4,076,842. Zeolite ZSM-35 and the conventional preparation thereof are described in U.S. Patent 4,016,245. Another preparation of ZSM-35 is described in U.S. Patent 4,107,195. ZSM-48 and the conventional preparation thereof is taught by U.S. Patent 4,375,573.

Although the term "zeolites" encompasses materials containing silica and alumina, it is recognized that the silica and alumina portions may be replaced in whole or in part with other oxides. More particularly, GeO_2 is an art-recognized substitute for SiO_2. Also, B_2O_3, Cr_2O_3, Fe_2O_3, and Ga_2O_3 are art-recognized replacements for Al_2O_3. Accordingly, the term zeolite as used herein shall connote not only materials containing silicon and, optionally, aluminum atoms in the crystalline lattice structure thereof, but also materials which contain suitable replacement atoms for such silicon and/or aluminum. On the other hand, the term aluminosilicate zeolite as used herein shall define zeolite materials consisting essentially of silicon and aluminum atoms in the crystalline lattice structure thereof, as opposed to materials which contain substantial amounts of suitable replacement atoms for such silicon and/or aluminum.

Particularly preferred zeolites which can be used in accordance with the present process for converting paraffins include zeolites having the structure of ZSM-5 and ZSM-11. In addition to patents mentioned hereinabove, ZSM-5 is described in U.S. Patent 3,702,886. ZSM-11 is structurally similar to ZSM-5. In view of the structural similarities between ZSM-5 and ZSM-11, these two zeolites have been observed to have similar catalytic properties in the conversion of various hydrocarbons. ZSM-11 is described in U.S. Patent 3,709,979. It is to be understood that references in the following description to ZSM-5 or ZSM-11 are also applicable to the medium-pore zeolites in general, i.e. those zeolites having a Constraint Index of between 1 and 12.

Zeolites suitable for use in the present paraffin conversion process can be used either in the as-synthesized form, the alkali metal form and hydrogen form or another univalent or multivalent cationic form. These zeolites can also be used in intimate combination with a hydrogenating component such as tungsten, vanadium, molybdenum, rhenium, nickel, cobalt, chromium,

manganese, or a noble metal such as platinum or palladium where a hydrogenation-dehydrogenation function is to be performed. Such components can be exchanged into the composition, impregnated therein or physically intimately admixed therewith. Such components can be impregnated in or on to a zeolite such as, for example, by, in the case of platinum, treating the zeolite with a platinum metal-containing ion. Suitable platinum compounds for this purpose include chloroplatinic acid, platinous chloride and various compounds containing the platinum amine complex. Combinations of metals and methods for their introduction can also be used.

Although the zeolites suitable for use in the process of the present invention may optionally include various elements ion exchanged, impregnated or otherwise deposited thereon, it is preferred to use zeolites in the hydrogen form, wherein the pore space of these zeolites is free of intentionally added elements other than hydrocarbonaceous deposits, particularly those elements which are incorporated into the zeolite pore space by an ion exchange or impregnation treatment. Thus, these zeolites can be free of oxides incorporated into the zeolites by an impregnation treatment. Examples of such impregnated oxides include oxides of phosphorus as well as those oxides of the metals of Groups IA, IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, or VB of the Periodic Chart of the Elements (Fisher Scientific Company, Catalog No. 5-702-10). The impregnation of zeolites with such oxides is described in the Forbus et al. U.S. Patent 4,55,394, particularly the passage thereof extending from column 8, line 42 to column 9, line 68. The hydrogen form of zeolites may be prepared by calcining the as-synthesized form of the zeolites under conditions sufficient to remove water and residue of organic directing agents, if any, ion exchanging the calcined zeolites with ammonium ions and calcining the ammonium exchanged zeolites under conditions sufficient to evolve ammonia.

Medium-pore zeolite catalysts such as synthetic ZSM-5 or ZSM-11, when employed as part of a catalyst in a hydrocarbon conversion process, should be dehydrated at least partially. This can be done by heating to a sufficient temperature, e.g. in the range of from 65°C to 550°C in an inert atmosphere, such as air, nitrogen, etc., and at atmospheric or subatmospheric pressures for between 1 and 48 hours. Dehydration can be performed at lower temperature merely by placing the zeolite in a vacuum, but a longer time is required to obtain a particular degree of dehydration. Organic materials, e.g. residues of organic directing agents, can be thermally decomposed in the newly synthesized zeolites by heating same at a sufficient temperature below the temperature at which the significant decomposition of the zeolite framework takes place, e.g from 200°C to 550°C, for a sufficient time, e.g. from 1 hour to 48 hours.

Zeolites may be formed in a wide variety of particle sizes. Generally speaking, the particles can be in the form of a powder, a granule, or a molded product, such as extrudate having particle size sufficient to pass through a 2 mesh (Tyler) screen and be retained on a 400 mesh (Tyler) screen. In cases where the catalyst is molded, such as by extrusion, the crystalline material can be extruded before drying or dried or partially dried and then extruded.

In the case of the present catalysts, the zeolites are incorporated with another material resistant to the temperatures and other conditions employed in certain organic conversion processes. Such matrix or binder materials include active and inactive materials and synthetic or naturally occurring zeolites as well as inorganic materials such as clays, silica and/or metal oxides, e.g. alumina. The latter may be either naturally occurring or in the form of gelatinous precipitates, sols or gels including mixtures of silica and metal oxides. Use of a material in conjuction with a zeolite, i.e. combined therewith, which is active, may enhance the

conversion and/or selectivity of the catalyst in certain organic conversion processes. Inactive materials suitably serve as diluents to control the amount of conversion in a given process so that products can be obtained economically and orderly without employing other means for controlling the rate of reaction. Frequently, crystalline silicate materials have been incorporated into naturally occurring clays, e.g. bentonite and kaolin. These materials, i.e. clays, oxides, etc., function, in part, as binders for the catalyst. It is desirable to provide a catalyst having good crush strength because the catalyst may be subjected to rough handling which tends to break the catalyst down into powder-like materials which cause problems in processing.

Naturally occurring clays which can be composited with zeolites include the montmorillonite and kaolin families which include the subbentonites, and the kaolins commonly known as Dixie, McNamee, Georgia and Florida clays, or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite or anauxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification.

In addition to the foregoing materials, zeolites can be composited with a porous matrix material such as silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, as well as ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. The matrix can be in the form of a cogel. A mixture of these components could also be used.

The catalyst used in the present paraffin conversion process may be in a variety of forms including in the form of extrudates or spray-dried microspheres. The Bowes U.S. Patent 4,582,815 describes a silica and ZSM-5 extrudate. The Chu et al. U.S. Patent 4,522,705 describes spray-dried microspheres containing

alumina and ZSM-5. This form of microspheres, as opposed to extrudates, is preferred when the catalyst is to be contacted with the hydrocarbon feedstock in a fluid bed reactor.

Hydrocarbon feedstocks which can be converted according to the present process include various refinery streams including coker gasoline, light F.C.C. gasoline, as well as C_5 to C_7 fractions of straight run naphthas and pyrolysis gasoline. Particular hydrocarbon feedstocks are raffinates from a hydrocarbon mixture which has had aromatics removed by a solvent extraction treatment. Examples of such solvent extraction treatments are described on pages 706-709 of the Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition, Vol. 9, 706-709 (1980). A particular hydrocarbon feedstock derived from such a solvent extraction treatment is a Udex raffinate. The paraffinic hydrocarbon feedstock suitable for use in the present process may comprise at least 75 percent by weight, e.g. at least 85 percent by weight, of paraffins having from 2 to 12, preferably from 5 to 10 carbon atoms.

The paraffinic hydrocarbons may be converted under sufficient conditions including, e.g. a temperature of from 100°C to 700°C, a pressure of from 10 kPa (0.1 atmosphere) to 6080 kPa (60 atmospheres), a weight-hourly space velocity of from 0.5 to 400 and a hydrogen/hydrocarbon mole ratio of from 0 to 20. Suitable reaction conditions are also described in the aforementioned Cattanach U.S. Patent 3,756,942.

The catalyst used in the present paraffin conversion process may have a relatively low acid catalytic activity for a medium-pore zeolite catalyst. More particularly, these catalysts may have an alpha value of from 2 to 12, preferably from 5 to 10. When alpha value is referred to herein, it is noted that the alpha value is an approximate indication of the catalytic cracking activity of the catalyst compared to a standard catalyst and it gives the relative rate constant (rate of normal hexane conversion

per volume of catalyst per unit time). It is based on the activity of the highly active silica-alumina cracking catalyst taken as an alpha of 1 (Rate Constant = 0.016 sec^{-1}). Alpha tests are described in U.S. Patent 3,354,078 and in The Journal of Catalysis, IV, 522-529 (1965). Alpha tests are also described in J. Catalysis, 6, 278 (1966) and J. Catalysis, 61, 395 (1980) with experimental conditions of the test used herein including a constant temperature of 538°C and a variable flow rate as described in J. Catalysis 61, 395.

In accordance with the present process, the present hydrocarbon feedstock is converted under sufficient conditions to convert at least 90 percent by weight (e.g. at least 93 percent by weight) of the paraffins present into different hydrocarbons. These different hydrocarbons may comprise at least 90 percent by weight (e.g. at least 95 percent by weight) of the sum of C_6-C_8 aromatics, C_2-C_4 olefins, C_9+ aromatics and C_1-C_3 paraffins. The conversion of paraffins may be less than 100 percent, e.g. 99 percent by weight or less. Conversion of paraffins under excessively extreme conditions may cause excessive coke formation on the catalyst and may result in the further conversion of C_2-C_4 olefins and C_6-C_8 aromatics into less desired products. The conversion products may include at least 68 percent by weight of the sum of C_6-C_8 aromatics plus C_2-C_4 olefins.

The catalyst suitable for use in accordance with the present invention may have an alpha value of greater than 5 or less than 33, preferably 10 to 20.. This narrow range of alpha values may be achieved in a variety of ways. For example, the active zeolite portion of the catalyst could be blended with sufficient amounts of inert binder material. Thus, the ratio of binder to zeolite may be at least 70:30, preferably at least 95:5. Another way of achieving an alpha value within the desired range is to subject a more active catalyst, e.g. having an alpha value of at least 50 in the catalytically activated form, to sufficient

deactivating conditions. Examples of such deactivating conditions include steaming the catalyst, coking the catalyst and high temperature calcination of the catalyst, e.g. at a temperature of greater than 700°C. It may also be possible to partially deactivate the catalyst by subjecting the catalyst to a sufficient amount of a suitable catalyst poison. Catalysts which have been deactivated in the course of organic compound conversions, particularly where the catalyst has been subjected to conditions of high temperature, coking and/or steaming, may be useful. Examples of such organic compound conversions include the present conversion of C_2-C_{12} paraffins and the conversion of methanol into hydrocarbons.

It may also be possible to use zeolites which are intrinsically less active by virtue of having a high silica to alumina molar ratio of, e.g. greater than 100. However, since ZSM-5 may be more difficult to prepare at such higher silica to alumina ratios, particularly in the absence of an organic directing agent, it may be more desirable to use a more active form of ZSM-5, e.g. having a silica to alumina molar ratio of 100 or less. Even though the alpha value of the activated form of such ZSM-5 may be rather high, the alpha value of the bound catalyst may be made much lower by one or more of the above-mentioned techniques. For example, ZSM-5 prepared from a reaction mixture not having an organic directing agent and having a framework silica to alumina molar ratio of 70:1 or less may be bound with an inert binder at a binder:ZSM-5 weight ratio of 75:25, and the bound catalyst could be subjected to sufficient deactivating conditions involving high temperature calcination and/or steaming of the catalyst.

The catalyst suitable for use in accordance with the present invention may be free of intentionally added gallium. More particularly, the only gallium in the catalyst may result from unavoidable trace gallium impurities either in the binder or in the sources of silica and alumina used to prepare the zeolite.

The paraffin conversion process of the present invention may take place either in a fixed bed or a fluid bed of catalyst particles. Particularly, when a fluid bed process is used, the process parameters may be adjusted to cause partial deactivation of the catalyst, thereby enabling the increase in selectivity to C_6-C_8 aromatics and C_2-C_4 olefins. In such a fluid bed process, the paraffinic feedstock is contacted with a fluid bed of catalyst, whereby conversion products are generated. Lighter hydrocarbons can be separated from the catalyst by conventional techniques such as cyclone separation and, possibly, steam stripping. However, the dense hydrocarbonaceous deposit (e.g. coke) which forms on the catalyst is more difficult to remove. This hydrocarbonaceous deposit may be removed by transporting the catalyst to a separate regenerator reactor, wherein the hydrocarbonaceous deposit is burned off the catalyst. The regenerated catalyst may then be returned to the fluid bed reactor for further contact with the paraffinic feedstock.

It is quite apparent from this process that the catalyst is constantly subjected to conditions which tend to deactivate the catalyst. These conditions include steaming, high temperatures and coking. Normally, the operator of such a process would tend to minimize the rate of catalyst deactivation by controlling parameters such as the amount and temperature of steam in the strpping section, the residence time of the catalyst in the various stages, the rate of catalyst recycle and the temperature in the regenerator. Some deactivation of the catalyst is inevitable, but the activity of the overall catalyst inventory may be maintained near its original level by periodically removing aged catalyst from the system and by replacing this aged catalyst with fresh catalyst. However, in view of the present discovery of improved product selectivity as a result of using catalyst having a controlled, relatively low acid activity value, the process operator may now be motivated to use the process parameters at his disposal to optimize catalyst aging while at the

same time refraining from replacing aged catalyst with fresh catalyst at a rapid rate. In such a process, the operator could monitor the rate of catalyst deactivation by reducing the weight hourly space velocity (WHSV) of the feed, while maintaining a constant rate of conversion under otherwise constant conditions. As activity of the catalyst decreases the operator would also observe an improved selectivity to C_6-C_8 aromatics and C_2-C_4 olefins.

EXAMPLES

A mixture of C_5-C_{10} aliphatic hydrocarbons rejected from the Udex extraction of refinery light reformate (Udex raffinate) was converted over a fluid bed catalyst incorporating 25 wt.% of a ZSM-5 zeolite. The catalyst composites had alpha activities, measured by the standard n-hexane cracking test shown below. The conversion reaction was carried out at approximately 621°C (1150°F), 0.5 WHSV raffinate (based on total catalyst weight) and atmospheric pressure.

TABLE 1

UDEX Raffinate Composition

Component	Wt.%
C_4 paraffins	0.09
C_5 paraffins	3.87
C_5 olefins and naphthenes	0.87
C_6 paraffins	51.44
C_6 olefins and naphthenes	3.06
C_7 paraffins	32.33
C_7 olefins and naphthenes	0.31
C_8+ PON	3.80
Benzene	0.16
Toluene	3.98
Xylenes	0.09
Other Properties:	
Specific gravity:	0.674
Clear (R+O) octane number:	66.5

	Example 1	Example 2	Example 3
Catalyst Alpha Activity	5	9	33
TOS, days	0.4	0.3	0.4
PON Conv., %	91.3	92	90.2
Net Yields From Feed			
PON, Wt.%			
H_2	1.2	1.4	1.8
CH_4	18.3	14.9	15.0
C_2H_4	12.1	17.1	15.2
C_2H_6	13.0	7.5	10.1
C_3H_8	4.9	3.5	4.9
C_3H_6	14.7	18.0	13.4
C_4H_8	6.1	6.2	4.3
Benzene	9.2	10.3	12.2
Toluene	6.8	7.2	8.2
C_8 Aromatics	2.1	2.5	3.9
C_2-C_4 Olefins	32.9))51.0	41.3))61.3	32.9))57.4
C_6-C_8 Aromatics	18.1)	20.0)	24.5)

Changes and modifications in the specifically described embodiments can be carried out without departing from the scope of the invention which is intended to be limited only by the scope of the appended claims.

CLAIMS:

1. A process for converting a hydrocarbon feedstock comprising at least 75 percent by weight of a mixture of at least two different paraffins having from 2 to 12 carbon atoms comprising the steps of contacting the hydrocarbon feedstock under conversion conditions with a composite catalyst comprising (1) a binder and (2) a zeolite having a Constraint Index of between 1 and 12, the zeolite being an aluminosilicate, the composite catalyst having an alpha value of greater than 5 and less than 33, whereby at least 90 percent by weight of the paraffins are converted to a hydrocarbon product mixture.

2. The process of claim 1 wherein the zeolite has the structure of at least one selected from ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35 and ZSM-48.

3. The process of claim 1, wherein the activated form of the fresh catalyst as initially prepared has an alpha value of at least 50 and the fresh catalyst is partially deactivated by subjecting the fresh catalyst to sufficient deactivating conditions to achieve an alpha value of greater than 5 and less than 33 for the catalyst.

4. The process of claim 1, wherein the fresh catalyst is partially deactivated by steaming the catalyst, coking the catalyst, calcining the catalyst at a temperature of greater than 700°C, or combinations of the steaming, coking and calcining.

5. The process of claim 1, wherein the catalyst is free of intentionally added gallium.

6. The process of claim 1, wherein the catalyst is prepared by combining a binder material with an aluminosilicate, the binder consisting essentially of alumina or silica in combination with alumina, the aluminosilicate zeolite having a silica to alumina ratio of less than 100.

7. The process of claim 6, wherein the zeolite is prepared from an aqueous reaction mixture comprising sources of silica and alumina, the reaction mixture being free of an organic directing agent.

8. The process of claim 1, wherein the composite catalyst has an alpha value of between 10 and 20.

9. The process of claim 7, wherein the weight ratio of binder to zeolite is at least 95:5.

10. The process of claim 1, wherein the hydrocarbon feedstock is a raffinate from a solvent extraction treatment which removes aromatics from a hydrocarbon feedstream.

11. The process of claim 10, wherein the hydrocarbon feedstock is a Udex raffinate.

12. The process of claim 1, wherein the hydrocarbon feedstock is contacted with the composite catalyst in a fluid bed reactor.

13. The process of claim 1, wherein the reaction conditions include a temperature of from 400°C to 700°C, a pressure of from 10 to 6080 kPa, a weight hourly space velocity of from 0.1 to 400 and a hydrogen/hydrocarbon mole ratio of from 0 to 20.

14. The process of claim 1, wherein less than 100 percent of the paraffins are converted.

15. The process of claim 1, wherein the zeolite has the structure of ZSM-5.

16. The process of claim 1, wherein the hydrocarbon product mixture comprises at least 55 percent by weight of the sum of C_6-C_8 aromatics and C_2-C_4 olefins.

17. The process of claim 1, wherein the zeolite is in the hydrogen form and the zeolite is free of metal oxides impregnated thereon.

18. The process of claim 1 wherein the composite catalyst has an initial alpha value of at least 50 prior to contact

with the feedstock, whereby at least 90 percent by weight of the paraffins are converted to a product mixture, and whereby a hydrocarbonaceous deposit is formed on the catalyst;

the composite catalyst is separated from hydrocarbons, with C_6-C_8 aromatics and C_2-C_4 olefins being recovered from the product mixture;

the hydrocarbonaceous deposit from the separated composite catalyst is removed by contacting the separated catalyst with a gas comprising oxygen under conditions sufficient to oxidize the hydrocarbonaceous deposit;

the separated catalyst is recycled to the fluid bed, the process further comprising;

the process parameters being adjusted to cause partial deactivation of the catalyst introduced into the fluid bed to achieve an average alpha activity of composite catalyst in the fluid bed greater than 5 and less than 33; and

the process being continued so that the selectivity to the sum of C_6-C_8 aromatics and C_2-C_4 olefins is increased.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/00933

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^5: C 10 G 45/64

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC^5	C 10 G

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	US, A, 4788364 (HARANDI) 29 November 1988 see claims 15,19,21,24,26,30,31; column 3, lines 24-42; column 4, lines 43-45	1,2,6,8,10, 11-15
A	US, A, 4341748 (PLANK et al.) 27 July 1982 see column 3, line 53 - column 6, line 48 cited in the application	1,6,7,15

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
11th May 1990	18. 06. 90
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	F.W. HECK

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9000933
SA 34935

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 12/06/90
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4788364	29-11-88	None	
US-A- 4341748	27-07-82	US-A- 4199556	22-04-80
		US-A- 4175114	20-11-79

EPO FORM P0479

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82